A simple self-powered sensor for the detection of D2O and other isotopologues of liquid water

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Abstract

We report the development and evaluation of a simple, inexpensive sensor capable of detecting liquid D$_2$O and other isotopologues of liquid water through the measurement of electrical signals generated from a nano-porous alumina film. This electrical output, consisting of a sharp voltage pulse followed by a separate broad voltage pulse, is present during the application of microliter volumes of liquid. The amplitude and temporal characteristics of these pulses have been combined to enable four diagnostic parameters used for the sensing of D$_2$O and H$_2$O$^{18}$O. The sensing mechanism is based on spatially localized variations in the surface potential of alumina, induced by isotopically substituted water molecules, combined with the effect of isotopic composition on charge transfer to the sensor. As a proof-of-concept demonstration, a sensing system has been developed that provides real-time detection of liquid D$_2$O in a stand-alone system.

Introduction

Heavy water (D$_2$O) is employed in the field of chemical analysis, spectral characterization and biomedical systems$^{1-4}$. Important applications include using heavy water as a tracer to study the mechanism of respiration and photosynthesis$^{5-8}$, for fabricating the isotopically substituted organic compounds$^{6,7}$, and as solvents for nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy$^{4,9,10}$. Heavy water has also been shown to be effective in the hypothermic preservation of the pancreas$^{11,12}$. Heavy water is also fundamental to the operation of heavy water reactors$^{13-16}$ so that a means of sensing the presence of D$_2$O or of distinguish D$_2$O from H$_2$O is needed for nuclear safety.

Since D$_2$O differs from H$_2$O only by the substitution of deuterium atoms, the physical and chemical properties of heavy water are quite like regular water$^{17-19}$. They also have similar visual appearance, so that the presence of D$_2$O can only be detected through sophistical tests such as atomic absorption spectroscopy, mass spectrometry$^{16}$, nuclear magnetic resonance spectroscopy$^{20,21}$, and infrared spectroscopy$^{22}$. These analytical techniques suffer from several limitations including the necessity of transferring samples to a fixed site, the use of expensive specialized analytical instruments, and complex analytical protocols requiring trained technicians. Recently, optical sensors have been developed for distinguishing between H$_2$O and D$_2$O via the physical interaction of the sensor with D$_2$O and H$_2$O$^{23-28}$, or the detection of chemical variables such as acidity$^{29}$. In the nuclear industry, the basic heavy water sensing technology includes beetle detectors, dew point sensors, gamma spectrometry, tritium beta activity monitors$^{13-15}$. Despite these advances, heavy water sensors are not widely available. In this paper, we report on the real time detection of D$_2$O with a simple, low-cost, stand-alone electrical sensor that enables the detection of liquid D$_2$O at the point of generation which may include physically inaccessible locations. The method is based on the analysis of electrical signals generated when the sensing unit is exposed to microliter volumes of D$_2$O or other isotopologues of water such as H$_2$O$^{18}$O.
Result And Discussion

Heterogeneous surface potential and blockage of streaming potential

A streaming current produced as a liquid flows through a charged micro-/nano-channel, has been a common source for water-enabled electricity generation\textsuperscript{30–34}. The surface charge of a solid in liquid medium derives from the ionization or dissociation of surface groups, adsorption of ions from solution, or chemical substitution of surface groups\textsuperscript{35,36}. A positive surface charge on Al\textsubscript{2}O\textsubscript{3} nanoparticles arise through protonation effect Al-OH+H\textsuperscript{+}«AlOH\textsubscript{2}+\textsuperscript{30,35}. A schematic illustrating the surface charge of Al\textsubscript{2}O\textsubscript{3} nanoparticles and the interface between adjacent particles in nanoporous Al\textsubscript{2}O\textsubscript{3} structure (Supplementary Fig. 1) shows that counterions are distributed in the nanochannel forming a Stern layer and an electrical double layer (EDL) in the water medium\textsuperscript{37}. The generation of a streaming current is illustrated in Fig. 1a, which shows that this occurs as the mobile counterions in the EDL are dragged along with the water flow. The accumulation of the counterions at the downstream end of the channel results in a potential difference (streaming potential) between the top and the bottom of the nanochannel\textsuperscript{38–40}.

It has been found that the generation of a streaming current is strongly dependent on the presence of hydroxyl groups on the surface of Al\textsubscript{2}O\textsubscript{3}, as the coordinatively unsaturated surface Al ions in the Al\textsubscript{2}O\textsubscript{3} cell act as strong Lewis acid site (electron acceptor) for H\textsubscript{2}O adsorption producing surface -OH groups from the dissociation of water molecules\textsuperscript{41}. When the nanochannels contain a homogeneous distribution of surface function groups having the same composition and chemical bonding environment, the electric field remains constant along the nanochannel, causing the streaming potential to scale with the length of the channel. Exposure of the Al\textsubscript{2}O\textsubscript{3} surface to other reactive species, including the isotopologues of water, changes the composition of these surface functional groups resulting in the inhomogeneities in the electric field along the nanochannel. For example, a heterogeneous surface charge will occur when Al\textsubscript{2}O\textsubscript{3} nanoparticles containing surface -OH groups are exposed to D\textsubscript{2}O. This arises from exchange reactions such as Al-OH+D\textsuperscript{+}«Al-OHD\textsuperscript{+} and Al-OD+D\textsuperscript{+}« AlOD\textsubscript{2}+\textsuperscript{42–45}. As shown in Fig. 1b, the zeta potentials of Al\textsubscript{2}O\textsubscript{3} nanoparticles dispersed in H\textsubscript{2}O and D\textsubscript{2}O show different values indicating a varied surface charge. Under these conditions, the electric field along the channel surface is no longer uniform, resulting in the pressure gradients in the water flow, restricting the development of a streaming current. The streaming potential will decrease relative to that obtained from a pristine Al\textsubscript{2}O\textsubscript{3} surface containing only -OH groups.

Based on this principle, we have developed a sensor (Fig. 1c) based on a porous layer of α-Al\textsubscript{2}O\textsubscript{3} nanoparticles (NanoAmor, USA, 99.9% purity, ~200 nm diameter) that can be used to distinguish between D\textsubscript{2}O, H\textsubscript{2}O and other isotopologues of water. The Al\textsubscript{2}O\textsubscript{3} nanoparticles were used in “as-received” condition without subsequent chemical processing. Porous Al\textsubscript{2}O\textsubscript{3} films having a thickness of ~0.4 mm was fabricated using a direct compression method, during which a specific mass of Al\textsubscript{2}O\textsubscript{3} nanoparticles was compressed to form a film. XRD and EDS characterization of the Al\textsubscript{2}O\textsubscript{3} and its microstructure are shown in Supplementary Figs. 2 and 3. These measurements show that the nanoparticles are corundum, a-
Al$_2$O$_3$. SEM images of the surface and cross-section of a porous Al$_2$O$_3$ layer reveal that it contains an abundance of nanopores as required for the efficient production of a streaming current. As an example, open circuit voltages (OCVs) generated from the separate application of individual H$_2$O and D$_2$O droplets to the sensor as shown in Fig. 1c, are typically $\sim$3.3 V and $\sim$0.9 V (Fig. 1d), respectively, confirming that such a device shows different response to these two liquids.

**Electrical output characteristics**

To establish standard conditions, the OCV of the heavy water sensor with a structure consisting of a silver – point contact electrode / 0.4 mm thick Al$_2$O$_3$ nanoparticle layer / carbon paper was measured in response to the application of individual 8 mL water droplets at 10 min intervals. Droplets were applied at the same nominal location where the Ag electrode contacts the top surface of the Al$_2$O$_3$ film. As shown in Figs. 2a and 2b, the amplitude of the OCV initially increases with the number of droplets applied consecutively to the same location on the top of the middle layer near the silver electrode. The moisture inside the porous Al$_2$O$_3$ film reaches an equilibrium state after application of about five droplets after which the OCV reaches a stable value, as marked in Figs. 2a and 2b. As this process occurs, the surface of the Al$_2$O$_3$ nanoparticles is modified in response to exposure to water molecules. This reaction increases the concentration of surface Al-OH groups, enhancing the streaming potential. As found in our previous studies, an excess of water introduced in the Al$_2$O$_3$ film cause the collapse of the porous structure$^{30}$. In this work, the equilibrium state of water molecules adsorbed on the porous Al$_2$O$_3$ is reached after about five droplets, each with 8 µL volume and is applied at 10 min intervals. After establishment of the equilibrium (or steady) state, the maximum OCV for the detector on applying H$_2$O droplets can be high as 3.4 V while that for the detector using D$_2$O droplets is less than 1.0 V. The time dependence of the voltage pulses under these conditions is shown in Fig. 2c. While the time duration for both pulses is hundreds of microseconds, the pulse profiles are obviously different. The clear difference in amplitude of the OCV for application of the same quantity of liquid D$_2$O and H$_2$O is one characteristic that can be used to distinguish between D$_2$O and H$_2$O. This diagnostic is evident even when the OCV is measured with a digital multimeter (DMM) at a sampling rate of $\sim$25 Hz.

Voltage measurement with a high sampling rate can reveal more detailed characteristics of the voltage pulses. Figs. 2d and 2e show one series of OCV pulses measured in the equilibrium state with an oscilloscope at a sampling rate of 200 KHz. This shows that, in fact, two voltage pulses are detected upon the application of one water droplet. The first pulse is sharp and narrow ($V_{\text{sharp}}$) while the second pulse is broad ($V_{\text{broad}}$) with a time duration of $\sim$200 ms. The $V_{\text{sharp}}$ signal can be associated with the initial contact of the liquid droplet with the silver electrode at the point of contact at the surface of the Al$_2$O$_3$ layer while $V_{\text{broad}}$ is the result of the streaming current as discussed above. This broad signal corresponds to that measured by the DMM (Figs. 2a and 2b). The rise time of $V_{\text{broad}}$, which is determined by the spread of water in the porous medium, is as short as $\sim$20 ms indicating the high hydrophilicity of the porous alumina film. The maximum and average amplitude of the OCV generated in the equilibrium
state from five sensors are compared in Fig. 2h and Supplementary Fig. 4. It is found that $V_{\text{broad}}$ generated from application of H$_2$O droplets has a larger amplitude than that generated from the application of D$_2$O droplets for all the measured sensors, confirming that the amplitude of $V_{\text{broad}}$ measured under standardized conditions is a primary diagnostic for the presence of D$_2$O.

The relationship between $V_{\text{sharp}}$ and $V_{\text{broad}}$ also reflects how the OCV changes on exposure to H$_2$O or D$_2$O. The amplitude ratio of $V_{\text{sharp}}/V_{\text{broad}}$ for each droplet in a series of consecutive droplet applications in the equilibrium state has been calculated using the OCVs in Figs. 2d and 2e and is shown in Fig. 2i. Supplementary Fig. 5 shows the amplitude ratio calculated from five sensors. The $V_{\text{sharp}}/V_{\text{broad}}$ obtained from the application of H$_2$O droplets is always $< 1$ while that from the application of D$_2$O droplets is generally $> 1$. This ratio can then be regarded as another reliable diagnostic parameter to distinguish between H$_2$O and D$_2$O.

A fast Fourier transform (FFT) of the $V_{\text{broad}}$ signal over a time scale of 0-0.15 s (see Figs. 2d and 2e) has been used to reveal the frequency components associated with this signal. These frequency components can be associated with the dynamics of the physical and chemical processes occurring in the detector. As shown in Supplementary Fig. 6, Figs. 2f and 2g, the frequency spectrum obtained from both $V_{\text{broad}}$ generated from the application of H$_2$O droplets and that from D$_2$O droplets is characterized by a direct current (DC) component and a range of alternating frequency components extending to 100 kHz. The amplitude of the DC components originating from the application of H$_2$O droplets is $\sim 10$ dBV, which is much higher than that from the application of D$_2$O droplets (-5 dBV). The amplitude of the alternating current (AC) components from the H$_2$O-triggered voltage gradually decreases as the frequency increases from $\sim 6$ Hz to $\sim 10$ kHz, and then stabilizes at $\sim -72$ dBV for the AC components at higher frequency. This transition stage from the DC component to the AC components with a stabilized voltage is faster for the D$_2$O-induced voltage, as shown by the dashed rectangle in Figs. 2f and 2g. The amplitude stabilized at $\sim -75$ dBV when the AC components exceed $\sim 2500$ Hz. The difference in the transition stage from the DC component to the AC components shows that the low-frequency AC component accounts for a larger proportion of the H$_2$O-induced voltage signal, which makes $V_{\text{broad}}$ from H$_2$O droplets closer to a step function. These differences in the FFT results can be regarded as an auxiliary diagnostic tool for detection of the presence of D$_2$O.

Further details on the time evolution of $V_{\text{sharp}}$ can be obtained with a sampling rate of 1 GHz. Figs. 3a and 3b show the time dependence of $V_{\text{sharp}}$ generated from two different sensors when H$_2$O and D$_2$O droplets are applied. $V_{\text{sharp}}$ pulses were measured after the equilibrium state of the moisture in the sensor had been established. Supplementary Fig. 7 shows $V_{\text{sharp}}$ generated from two more sensors. The time duration of these sharp voltage pulses is a few hundreds of microseconds for both the H$_2$O-triggered and D$_2$O-triggered signals. The time dependence of $V_{\text{sharp}}$ is as follows:
\[ V_{\text{sharp}}(t) = V_0 + V_d + V_g \left( e^{-t/\tau_g} - e^{-t/\tau_d} \right), \quad t \leq t_c \]  
\[ V_{\text{sharp}}(t) = V_0 + V_d e^{-\left(t-t_c\right)/\tau_d}, \quad t \geq t_c \]  

where \( V_0 \) is the offset, \( t_c \) is the time required to reach the peak amplitude of \( V_{\text{sharp}} \), \( \tau_g \) and \( \tau_d \) are growth and decay time constants as shown in Figs. 3c and 3d, \( V_g \) and \( V_d \) are obtained from the growth and decay amplitudes, respectively, after the fit. A plot of the maximum amplitude of \( V_{\text{sharp}} \) vs. the rise time \( t_c \) and \( V_g \) vs. \( \tau_g \) is shown in Figs. 3e and 3f following the sequential application of \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) droplets. The rise time of \( V_{\text{sharp}} \) generated from application of \( \text{D}_2\text{O} \) droplets was typically < 25 ms while that from application of \( \text{H}_2\text{O} \) droplets was found to be > 25 ms. The growth time constant generated from the application of \( \text{D}_2\text{O} \) is < 10 µs while that from the application of \( \text{H}_2\text{O} \) droplets is ≥ 10 µs. The derivative, \( \text{d}V_{\text{sharp}}/\text{d}t \), has also been calculated (Supplementary Fig. 8), and shows that there is a significant difference in the onset of \( V_{\text{sharp}} \) (or slope) generated from application of \( \text{H}_2\text{O} \) droplets and \( \text{D}_2\text{O} \) droplets. These results indicate that the time dependent characteristics of the rise of \( V_{\text{sharp}} \) can be taken as another diagnostic method to distinguish between \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \). The decay function shows a decay time constant of 19.5-134.6 µs and 77.8-191.8 µs for the \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) induced \( V_{\text{sharp}} \), respectively.

**Parameters affecting the electrical outputs**

The sensitivity of the two primary diagnostic parameters that enable the detection of \( \text{D}_2\text{O} \), namely i) the relative amplitude of \( V_{\text{broad}} \) produced from the application of \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) droplets, and ii) the ratio of the amplitude of \( V_{\text{sharp}} \) to that of \( V_{\text{broad}} \) in each measurement have been studied by changing the thickness of the \( \text{Al}_2\text{O}_3 \) layer, the composition of the electrode material and the operating temperature of the sensor. The effect of thickness on the OCV response of detector is shown in Supplementary Fig. 10 and Figs. 4a-b. These experiments show that the shape of \( V_{\text{broad}} \) varies slightly with film thickness, while the amplitude of \( V_{\text{broad}} \) from \( \text{H}_2\text{O} \) droplets is clearly higher than that from \( \text{D}_2\text{O} \) droplets for all the devices. For a \( \text{Al}_2\text{O}_3 \) layer thickness of 1.8 mm, the amplitude of \( V_{\text{broad}} \) generated from application of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) are both smaller than that observed in thinner layers (Supplementary Fig. 10). This occurs because this layer thickness is too large, preventing the establishment of an equilibrium state with a droplet volume of 8 µL and a time interval of 10 min. The amplitude ratio of \( V_{\text{sharp}}/V_{\text{broad}} \) is < 1 for the \( \text{H}_2\text{O} \)-induced and > 1 for the \( \text{D}_2\text{O} \)-induced voltage for all devices with thicknesses < 1.8 mm. The OCVs from other top/bottom electrode configurations such as Ag-\( \text{Al}_2\text{O}_3\)-Cu, Ag-\( \text{Al}_2\text{O}_3\)-ITO coated PET, Ag-\( \text{Al}_2\text{O}_3 \) layer-Pt and Cu-\( \text{Al}_2\text{O}_3 \)-carbon paper are shown in Supplementary Figs. 11-12 and Figs. 4c-d. The thickness of the \( \text{Al}_2\text{O}_3 \) layer was maintained at 0.4 mm. While there are variations in the amplitude of \( V_{\text{sharp}} \) and \( V_{\text{broad}} \) using different electrode materials, the average amplitude of \( V_{\text{broad}} \) from \( \text{H}_2\text{O} \) droplets (> 2 V) is always higher than that from \( \text{D}_2\text{O} \) droplets (< 2 V). The diagnostic properties of the ratio of the amplitude of
\( V_{\text{sharp}} \) to that of \( V_{\text{broad}} \) is also confirmed and is generally < 1 for H\(_2\)O-induced and > 1 for D\(_2\)O-induced voltage. We find that increasing the work temperature reduces the sensitivity of the sensor to the difference between D\(_2\)O and H\(_2\)O (Figs. 4e and 4f), but that the time interval between successive water droplets can be shortened to 2.5 min at 50 °C and 1.5 min at 75 °C (Supplementary Fig. 13). It is confirmed that the differences in the amplitude of \( V_{\text{broad}} \) and the \( V_{\text{sharp}}/V_{\text{broad}} \) ratio can be a strong diagnostic of the presence of D\(_2\)O when the sensor is operated at different temperatures (Figs. 4e and 4f). The amplitude of \( V_{\text{broad}} \) is improved significantly for the application of D\(_2\)O droplets when the sensor is at 75 °C.

The sensor can also be operated when the Al\(_2\)O\(_3\) nanoparticles are replaced with Al\(_2\)O\(_3\) nanowires (Supplementary Fig. 14). A similar response is obtained as \( V_{\text{broad}} \) from application of H\(_2\)O droplets has a higher amplitude than \( V_{\text{broad}} \) generated from the application of D\(_2\)O droplets. The ratio of the amplitude of \( V_{\text{sharp}} \) to the amplitude of \( V_{\text{broad}} \) also shows a difference between application of H\(_2\)O and D\(_2\)O droplets.

To evaluate the use of the Al\(_2\)O\(_3\) nanoparticle sensor with another isotopologue of water, the OCV obtained when droplets of H\(_2\)\(^{18}\)O were applied to a device using carbon as the top electrode. The response of the sensor is shown in detail in Supplementary Fig. 15.

**Work mechanisms**

The previous experiments demonstrate that the application of a single water droplet to the surface of the sensor results in the appearance of two distinct voltage pulses. The first pulse, \( V_{\text{sharp}} \), is prompt and appears when the water droplet first contacts the top electrode. The second pulse, \( V_{\text{broad}} \), is delayed by approximately 20-80 ms and can be associated with the flow of water into the Al\(_2\)O\(_3\) nanoparticle layer. \( V_{\text{broad}} \) then originates from a streaming current which appears from the interaction of water molecules with Al\(_2\)O\(_3\) nanoparticles and the flow of water through the nanochannels in the porous layer. As the flow of water, and the attendant streaming current, will be influenced by the viscosity, we have investigated the effect of water temperature on the electrical output of these sensors. As shown in Supplementary Fig. 16, the voltage amplitudes remain similar to those obtained at 25 °C when H\(_2\)O and D\(_2\)O droplets are applied to sensors held at 50 °C and 75 °C. As the viscosity changes over the temperature range between 25 °C and 75 °C\(^{46-49}\), these results show that this has little effect on \( V_{\text{broad}} \). The only change is that the overall duration of \( V_{\text{broad}} \) increases somewhat at higher temperature. This indicates that the temperature of the sensor and the viscosity of the water droplets may influence the electrical output characteristics of the device by affecting the diffusion rate without affecting the use of the amplitude of \( V_{\text{broad}} \) as a primary diagnostic for the detection of D\(_2\)O.

The nano porous Al\(_2\)O\(_3\) film before and after exposure to 100 uL of H\(_2\)O and D\(_2\)O were analyzed using XPS and Raman spectroscopy. The XPS results in Figs. 5a and 5b show that unprocessed Al\(_2\)O\(_3\) is
characterized by Al-O bonds, together with a small quantity of Al-OH bonding arising from atmospheric water. It contains Al-O bond and Al-OH/Al-OD bond for both Al₂O₃ that exposed to H₂O and D₂O, indicating that some hydroxyl groups are produced during the interaction of Al₂O₃ nanoparticles and H₂O/D₂O. The ratios of Al-OH/OD and Al-O are 0.83 and 0.63 for the H₂O-processed and D₂O-processed Al₂O₃ nanoparticles, respectively, which indicated that high-proportioned hydroxyl groups of Al-OH appear after the H₂O-exposure treatment than that (Al-OD) produced from D₂O-exposured alumina. This result is confirmed by the Raman spectra (Supplementary Fig. 17) which shows that the Al-OH/Al-O or Al-OD/Al-O ratio is 0.18, 0.34 and 0.21 for bare Al₂O₃, H₂O-treated Al₂O₃ and D₂O-treated Al₂O₃ nanoparticles, respectively. FTIR absorption spectra of the Al₂O₃ layer after exposure to H₂O and D₂O droplets are shown in Supplementary Fig. 18. The amount of Al-O bonded centers decreases after exposure to water droplets, as some Al-O bonds in the Al₂O₃ nanonetworks are converted into Al-OH/OD. This effect is more significant when the material is exposed to H₂O droplets compared to that exposed to D₂O.

It is evident that the introduction of isotopologues of water into the porous Al₂O₃ layer can influence the distribution of surface functional groups producing local inhomogeneities and variations in surface charge. The effects of this chemistry on the surface potential can be understood in terms of the simple physical model shown in Figs. 5c1-c3. As seen in Fig. 5c1, the original porous Al₂O₃ film contains a low concentration of Al-OH groups and exhibits a lower value of the zeta potential, z. z increases as the concentration of Al-OH groups rises when the first few water droplets are introduced into the system. Maximum surface coverage with Al-OH groups is achieved in the equilibrium state (see Fig. 2a) increasing the surface potential resulting in high OCV. The Al-OH surface groups obtained from a droplet of H₂O will bond in a similar chemical environment to that of pre-existing Al-OH groups obtained from atmospheric humidity. This ensures that the zeta potential is spatially uniform along the surface of the nanochannel (Fig. 5c2).

When the -OH in these surface groups is substituted with D atoms, or another isotopic species such as ¹⁸O, the surface composition becomes inhomogeneous, introducing localized regions where the potential varies from the average value for a surface containing only -OH groups (Fig. 5c3). In this case, these variations in the local potential act as “traps” that can attract negatively or positively charged ions depending on the local electric field gradient. For a flowing liquid containing charges, the existence of traps will act to reduce the streaming current, decreasing the amplitude of V broad. This effect will occur when D₂O is introduced into the system, resulting in the low OCVs observed compared to those obtained in -OH dominated Al₂O₃ surfaces (Fig. 2b).

To establish the origin of V sharp, experiments were carried out without the porous Al₂O₃ film. In this case, voltages were measured as H₂O and D₂O droplets were introduced to form a contact between the top metal rod electrode and the planar metal bottom electrode. As shown in Supplementary Fig. 19, V sharp still appears under these conditions without a porous Al₂O₃ layer, and the peak amplitude of V sharp is still larger for D₂O droplets than that for H₂O droplets. The relationship between the amplitude of the V sharp
and rise time ($t_c$ in the fitting function) is summarized in Fig. 5d and shows the clear difference in the rise time of $V_{\text{sharp}}$ between the H$_2$O and D$_2$O results found in the standard Ag-Al$_2$O$_3$-carbon sensor configuration. This suggests that $V_{\text{sharp}}$ arises from charges contained in the droplet and collected by the electrodes. To confirm this possibility, droplets were collected using a single metal electrode. The resulting $V_{\text{sharp}}$ signal (Fig. 5e and Supplementary Fig. 20) is like that seen in the other experiments, indicating that it arises from charges collected from the droplet. These charges likely originate from a ‘streaming current’ effect within the pipette tip surface and water flowing through the pipette$^{50}$ (Fig. 5f).

As the charging process is the same in all experiments, the amplitude of $V_{\text{sharp}}$ and rise time of $V_{\text{sharp}}$ are similar in the standard Ag-Al$_2$O$_3$-carbon sensor, in the metal-metal configuration and the configuration containing only one metal electrode (Fig. 3, Figs. 5d and 5e, respectively).

**Demonstration of application**

Finally, we develop a D$_2$O sensing system to illustrate this concept. The system includes three parts: a software programmed using LabVIEW, a data acquisition card of NI USB-6002 (maximum sampling rate is 50 kHz), and the sensor developed in this work. Two diagnostics, the amplitude of $V_{\text{broad}}$ (Demo 1) and time-dependent characteristics of $V_{\text{sharp}}$ (Demo 2) are selected for the demonstration. The application of water droplets to the sensor was kept with 8 µL volume and 10 min interval, and wo separate sensors are tested. With a sampling rate of 200 Hz, $V_{\text{broad}}$ signals were acquired as shown in Figs. 6b and 6c and Supplementary Movies 1-2, which indicate the presence of H$_2$O and D$_2$O, respectively. When set the sampling rate at 50 kHz, the $V_{\text{sharp}}$ and the corresponding calculated $dV_{\text{sharp}}/dt$ can be acquired. While the $dV_{\text{sharp}}/dt$ is smaller than that presented in Supplementary Fig. 8 since the sampling rate of the acquisition card is too low to acquire the peak voltage of $V_{\text{sharp}}$, it still shows differences by application of H$_2$O (<20000) and D$_2$O (>20000) and sensed the presence of H$_2$O and D$_2$O, as shown in Figs. 6d and 6e, Supplementary Movies 3-4. These demonstrations are direct validations that the heavy water sensor developed in this work can be used to distinguish between H$_2$O and D$_2$O. It is suggested that four diagnostics can be developed into one integrated system to improve the detection accuracy for a practical application. These results lay the foundation for the development of electrical signals-based heavy water sensor as a new kind of self-powered, simple-operated and low-cost sensing strategy.

**Conclusion**

In summary, an electrical signals-based heavy water sensor has been developed using nano-porous Al$_2$O$_3$ network as the sensing material. Two voltage pulses ($V_{\text{sharp}}$ and $V_{\text{broad}}$) were sequentially generated as one water droplet was applied to the sensor, characteristics of which are developed into diagnostics to distinguish between H$_2$O and D$_2$O. $V_{\text{broad}}$ originates from the streaming potential generated from water flowing through the Al$_2$O$_3$ film and $V_{\text{sharp}}$ derives from the charge separation process as droplet is dispersed from the pipette tip. The sensing mechanism is based on spatially localized variations in the surface potential of alumina, induced by isotopically substituted water molecules, combined with the
effect of isotopic composition on charge transfer to the sensor. This detection concept using the electrical output signal of a device is verified by changing Al$_2$O$_3$ film thickness, electrode pairs, work temperatures or even the sensing materials. A sensing system using the amplitude of $V_{\text{broad}}$ and the time dependent characteristics of $V_{\text{sharp}}$ has been developed which successfully sense the presence of H$_2$O and D$_2$O. It’s also supposed that this method is appliable to D$_2$O leakage detection and D$_2$O purity detection, which will be presented in our future work.

**Methods**

**4.1. Preparation of the heavy water sensor assembly**

A certain mass of Al$_2$O$_3$ nanoparticles (NanoAmor, USA) with a diameter of $\sim$200 nm was put into the mould (diameter is 10 mm), after which the mould was compressed using a universal tensile machine at a pressure of 6 MPa and a compress rate of 10 mm/min. The thickness of the alumina layer was typically 0.4 mm, which is made from a mass of 30 mg of Al$_2$O$_3$ nanoparticles, unless specifically noted. The sensor is assembled by connecting the Al$_2$O$_3$ film to a porous carbon paper as bottom electrode and a top Ag rod (14 AWG, pure 99.99% silver) electrode contacting the top of the film. The diameter of Ag rod is 2 mm and a tip was ground out using sand paper. Deionized water (DI, H$_2$O) and heavy water of D$_2$O (Deuterium oxide, 99.9 atom % D) ordered from Sigma-Aldrich were apply to the surface of Al$_2$O$_3$ film where Ag electrode is placed in the form of droplets. The droplets were dispensed using a micropipette. Water volume of each droplet was 8 µL and the time interval between droplets were set as 10 min unless noted.

Other configurations have also been fabricated to verify the feasibility of this method. For example, a series of parameters have been changed including the Al$_2$O$_3$ layer thickness, other electrode pairs, work temperatures and sensing materials. The Al$_2$O$_3$ layer thickness was controlled by varying the weight of Al$_2$O$_3$ nanoparticles, and the relationship between layer thickness and mass of nanoparticles is shown in Supplementary Fig. 9. The bottom carbon electrode was replaced with Cu sheet, ITO-coated PET and Pt-coated silicon wafer and the top electrode was replaced with Cu wire (24 AWG, 0.5 mm in diameter) to fabricate different sensors. The work temperatures were controlled by putting the device on hot plate with set temperature. Both H$_2$O and D$_2$O was processed in a water bath with set temperatures of 50 °C and 75 °C to produce viscosity variations. Al$_2$O$_3$ nanowires (NW, 2–6 nm × 200–400 nm) ordered from Sigma-Adrich was selected as one replaceable material and the electrical signals of Ag-Al$_2$O$_3$ NW-C configuration was also measured when apply water droplets to the sensor. To further confirm the feasibility of our proposed method to distinguish different water types, H$_2^{18}$O (99 atom%) ordered from Sigma-Adrich was applied to the sensor to measure the electrical output.

**4.2. Characterization**
X-ray diffraction (XRD, DX-2700) and selected-area electron diffraction (SAED) were used to identify phase structure. Scanning electron microscopy (SEM, UltraPlus FESEM, Carl Zeiss AG CO., LTD., DE) equipped with an energy dispersive spectrometer (EDS) was used to observe and analyze the microstructure of the Al₂O₃ NPs, and surface and cross-section of the compressed Al₂O₃ film. Optical microscopy (OM) was adopted to obtain the cross-sectional images of the Al₂O₃ film, which was used to measure the film thickness. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (633 nm laser), FTIR (8400S spectrometer) were used to analyze the composition of the Al₂O₃ NPs. The zeta potential of Al₂O₃ nanoparticles in H₂O and D₂O was measured with a potentiometer.

### 4.3. Electric Measurements And Analysis

All the voltage measured in this work corresponded to the open-circuit voltage (U_{OC}). Droplets of 8 µL H₂O and D₂O were applied to the surface of the Al₂O₃ surface where the Ag electrode was placed at a time interval of 10min. Separate sensors were used for the measurement when apply these two kinds of water. The initial main diagnostic of the difference in the amplitude of voltage was recorded using an Agilent 34410A digital multimeter. The sampling rate is ~ 25 Hz and the input impedance is 10 MΩ. This diagnostic is effective when the sampling time of the measuring equipment is in the range from several milliseconds to tens of milliseconds. Further three diagnostics were investigated with measurement conducted by Keysight InfiniiVisin DSOX2022A digital storage oscilloscope (Bandwidth is 200 MHz). A sampling rate of 200 kHz was used to analyze both the broad voltage signal and the sharp voltage signal, and sampling rate of 1GHz was used for the specific analysis of the V_{sharp}.

### Data Availability

The authors declare that the main data supporting the findings of this study are contained within the paper and the Supplementary files. All other relevant data are available from the corresponding author upon reasonable request.

### References


Declarations

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Author contributions

W.D. conceived the project. X.Z. and W.D. designed the research. X.Z. conducted the experiments, analyzed the data, drafted the manuscript. H.Y. programmed the software and demonstrate the application, helped on data analysis. S.Z. and T.G. helped on the Raman and FTIR and discussed some results. C.T., X.S. and J.F. provided suggestions on data analysis, device design and applications. W.D. and N.Z. discussed the results and revised the manuscript. C.T., J.F., W.D. and N.Z supervised the research. C.T. and N.Z. provided funding for this research.
Competing interest

The authors declare no competing interests.

Figures

Figure 1

Design basis of electrical output signals-based heavy water sensor. (a) Schematic illustrating the generation of electricity from the streaming potential. D represents the diameter of the nanochannel. The profile of the counterion density $r_x$ and the electrostatic potential $j_x$ are shown schematically. A streaming current ($I_s$) is generated when the counterions in the EDL are dragged by a pressure-driven flow ($p$-driven flow). (b) Zeta potential of Al$_2$O$_3$ nanoparticles dispersed in H$_2$O and D$_2$O. (c) An illustration of the physical structure of the heavy water sensor. An electrode is placed to form a point contact with the porous middle layer. The arrows indicate water flow through the porous film. (d) A comparison of the voltage generated from application of H$_2$O and D$_2$O droplets to the sensor after establishment of an equilibrium state.
Figure 2

(a) Characteristics of the OCV generated from repetitive application of 8 µL volume droplets of H$_2$O at 10 min intervals. (b) OCV for D$_2$O droplets under the same conditions. In both cases, the equilibrium state, indicated by the dashed line, is reached after application of five droplets. (c) Pulse shape of the OCV measured at a sampling rate of 25 Hz. (d) and (e) Characteristics of the OCV pulses measured with an oscilloscope at 200 kHz bandwidth showing the regions selected for FFT analysis. (f) and (g) FFT results from 0-20 kHz using the time dependent OCV between 0.0 and 0.15 s. Full FFT results are shown in Supplementary Fig. 6. (h) Comparison of the maximum OCV generated in the equilibrium state from different sensors. (i) Calculated ratio of the peak amplitudes of $V_{\text{sharp}}$ to $V_{\text{broad}}$. 
Figure 3

(a) and (b) The time dependence of $V_{\text{sharp}}$ on application of 8 mL volume droplets of H$_2$O and D$_2$O droplets. The detectors are in the equilibrium state as indicated in Figs. 2a and 2b. (c) and (d) Fits to the experimental data using eqns. 1 and 2. (e) Plot of the maximum amplitude of $V_{\text{sharp}}$ vs. rise time $t_c$. (f) Plot of $V_g$ vs. $\tau_g$. 
Figure 4

Influence of different parameters on the amplitude of $V_{\text{broad}}$ and the amplitude ratio of $V_{\text{sharp}}$ to $V_{\text{broad}}$ with application of H$_2$O and D$_2$O droplets to the system. (a) and (b) Varied Al$_2$O$_3$ layer thickness. (c) and (d) Different electrode pairs. The thickness of the porous Al$_2$O$_3$ film is 0.4 mm. (e) and (f) Different sensor temperatures. The thickness of the porous Al$_2$O$_3$ film was 0.4 mm, and the droplet temperature was initially 20 °C.
Figure 5

Sensing mechanism of the heavy water detector. (a) and (b) O1s and Al2p core spectra of the original porous Al₂O₃ film, Al₂O₃ film after exposure to H₂O and D₂O. (c1-c3) A schematic showing the differences in the quantity of surface function groups, surface charge density and characteristics of the surface potential. (d) Relationship between the maximum amplitude of V sharp and rise time of V sharp when apply the H₂O and D₂O droplets to the metal-metal system without a nanoparticles film. (e) Relationship between the maximum amplitude of V sharp and rise time of V sharp when apply the H₂O and D₂O droplets to the Ag and Cu electrode without a nanoparticles film and bottom electrode. (f) A schematic for the generation of V sharp.
Figure 6

Demonstration of the Al\(_2\)O\(_3\)-based heavy water sensor. (a) System developed for the sensor. (b) and (c) Voltage signals and displays showing a water type of H\(_2\)O and D\(_2\)O when the sampling rate is 200 kHz. (d) and (e) The collected voltage signals at a sampling rate of 50 kHz slope and the corresponding \(dV_{\text{sharp}}/dt\) indicate the presence of H\(_2\)O and D\(_2\)O, respectively.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- HeavywatersensorSupplementaryinformation.docx
- SupplementaryMovie1Demo1H2O.mp4
- SupplementaryMovie4Demo2D2O.mp4
• SupplementaryMovie2Demo1D2O.mp4
• SupplementaryMovie3Demo2H2O.mp4